

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-073681  
(43)Date of publication of application : 19.03.1996

---

(51)Int.Cl. C08L 23/16  
C08K 5/00

---

(21)Application number : 06-232323 (71)Applicant : BRIDGESTONE CORP  
(22)Date of filing : 01.09.1994 (72)Inventor : TOYOSAWA SHINICHI  
MASHITA SHIGEHIKO  
IMAI YASUSHI  
MATSUSE TAKAHIRO  
WAKANA YUICHIRO  
FUKAHORI YOSHIHIDE

---

## (54) ETHYLENE-PROPYLENE-BASED RUBBER COMPOSITION

### (57)Abstract:

PURPOSE: To obtain a low elastic composition uniformly containing a low-molecular material in good retaining properties, having excellent processability and slight oozing out, by blending a polymer network structure consisting essentially of ethylene and propylene with ethylene-propylene-based rubber.

CONSTITUTION: This composition is obtained by blending (A) a polymer network structure which is obtained by mixing (i) ≥60wt.% (especially preferably 90wt.%) of consisting essentially of ethylene and propylene with (ii) a low-molecular material having preferably ≤10,000 number-average molecular weight and composed of a softener, a plasticizer, a tackifier, an oligomer and a lubricant and retains the component (ii) between a three-dimensional continuous network skeleton comprising the component (i) with (B) ethylene-propylene-based rubber in the weight ratio of the component A/B of preferably 0.4-4.

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1](A) It is obtained when an ethylene content which uses ethylene and propylene as the main ingredients mixes a copolymer and low molecule material of 60 or more weight, An ethylene-propylene system rubber composition which mixes a polymers network structure object in which the above-mentioned low-molecular-weight material was held between three-dimensional continuation reticulated skeletons which consist of the above-mentioned copolymer, and (B) ethylene-propylene system rubber, and is characterized by things.

[Claim 2](A) The ethylene-propylene system rubber composition according to claim 1 whose weight ratio [ of an ingredient and the (B) ingredient ] (A)/(B) is 0.4-4.

---

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

**[Detailed Description of the Invention]****[0001]**

**[Industrial Application]**This invention relates to the ethylene-propylene system rubber composition of low elasticity which contains low molecule material with uniformly and sufficient holdout.

**[0002]**

**[Description of the Prior Art]**Conventionally, the ethylene propylene diene rubber (EPDM) which blended the third component with ethylene-propylene rubber (EPR) or EPR is widely used for uses, such as an object for vehicles, building-materials relations, an electric wire, and a cable.

**[0003]**By the way, although conventional EPR and EPDM lower an elastic modulus and mixing low molecule material so much in order to raise impact-absorbing ability may be performed, Since its holdout of low molecule material is weak, it tended to carry out bleeding of the low molecule material, and the ethylene-propylene rubber constituent which mixed low molecule material so much is difficult to distribute low molecule material uniformly, and also for this reason, was not able to obtain the target thing of the low elastic modulus.

**[0004]**In this invention, it was made in view of the above-mentioned situation.

Therefore, it aims at low molecule material's distributing uniformly, and holding low molecule material good, and the bleeding of low molecule material providing few ethylene-propylene system rubber compositions as much as possible.

**[0005]**

**[Means for Solving the Problem and its Function]**A result of having repeated examination wholeheartedly in order that this invention persons might attain the above-mentioned purpose, A polymers network structure object in which this low molecule material was held between three-dimensional continuation reticulated skeletons in which an ethylene content which uses ethylene and propylene as the main ingredients mixed a copolymer and low molecule material of 60 or more weight, and was formed with this copolymer is acquired, Subsequently, an ethylene-propylene system rubber composition obtained by mixing this polymers network structure object and ethylene-propylene rubber, For example, even if high formulation of the low molecule material is carried out to about 50% of the weight of the whole constituent, low molecule material distributes in a constituent uniformly, and moreover bleeding is hardly carried out, but it finds out that it is a low elastic modulus very much for this reason, and comes to make this invention.

[0006]Therefore, this invention is obtained when an ethylene content which uses (A) ethylene and propylene as the main ingredients mixes a copolymer and low molecule material of 60 or more weight, An ethylene-propylene system rubber composition which mixes a polymers network structure object in which the above-mentioned low-molecular-weight material was held between three-dimensional continuation reticulated skeletons which consist of the above-mentioned copolymer, and (B) ethylene-propylene system rubber, and is characterized by things is provided.

[0007]If it explains in more detail about this invention hereafter, an ethylene-propylene system rubber composition of this invention will mix (A) polymers network structure object and (B) ethylene-propylene system rubber, as mentioned above.

[0008]This polymers network structure object can be acquired by the ability to mix so that content of a copolymer of a (b) ingredient may serve as 30 or less % of the weight of a rate preferably in a copolymer and (\*\*) low molecule material which use (b) ethylene and propylene as the main ingredients.

[0009]This copolymer needs to be ethylene propylene system rubber (EPR) which uses ethylene and propylene as the main ingredients, and an ethylene content needs to be 60 % of the weight or more. An ethylene content is inferior to the physical properties of a polymers network structure object at less than 60 % of the weight. 65% of the weight or more, as for especially the maximum, although it is 70 % of the weight or more still more preferably, it is preferably preferred that it is 90 % of the weight 95% of the weight. A three-dimensional continuation reticulated skeleton Hard block parts, such as a crystal structure and condensation structure, It is preferred to have elasticity block parts with ones, such as amorphous structure, together, as for a degree of crystallinity of EPR, it is preferably preferred for this reason but most preferably that it is not less than 8% not less than 5% not less than 3%, and as for especially that maximum, it is preferred that it is 50% 60%. As for the melting point (Tm) of a polyethylene part showing the block nature of ethylene, it is desirable for not less than 30 \*\* not less than 25 \*\* to be not less than 35 \*\* still more preferably preferably with a differential scanning calorimetry (DSC). A number average molecular weight of a copolymer is [ 20000 or more / 30000 or more ] preferably good to use 40000 or more still more preferably.

[0010]The above-mentioned copolymer may contain copolymerization ingredients other than ethylene and propylene as occasion demands. It is good also as EPDM for 1,5-hexadiene, 1,4-hexadiene, a dicyclopentadiene, ethylidene norbornene, etc. to be mentioned, for example, and blend these third components with ethylene and propylene as this copolymerization ingredient. In this case, content of the third component has a desirable thing of the whole copolymer preferably considered as 3 to 10 % of the weight one to 15% of the weight.

[0011]As for a three-dimensional continuation reticulated skeleton concerning this invention, it is also effective to attach hydrophilic groups, such as a hydroxyl group, and lipophilic groups, such as a nitro group, to denaturalize the above-mentioned EPR and EPDM, and to change the characteristic depending on a use.

[0012]A three-dimensional continuation reticulated skeleton which comprises such a copolymer has a microstructure as shown in drawing 1. In drawing 1, a three-dimensional continuation reticulated skeleton which 1 becomes from the above-mentioned copolymer, and 2 are internal communicated space, and low molecule material later mentioned in this internal communicated space 2 is held. Here, that whose range is 1-50 micrometers is preferably desirable [ the pitch diameter d of the skeleton 1 / the range of 0.5-5 micrometers, and the pitch diameter D of a cell ] in drawing 1 preferably 80 micrometers or less 8 micrometers or less.

As for a void content, it is preferably desirable that it is 50 to 95% of range not less than 40%. [0013]On the other hand as a low molecule material held in the above-mentioned internal communicated space, a solid or a fluid may be sufficient, and it is usable in various things according to a use. If low molecule material is organic materials, the number average molecular weight is less than 20000, and what is 10000 or less and 5000 or less preferably is good. The following can be illustrated although there is no restriction in particular as a low molecule material.

\*\* Softener : various objects for rubbers, such as a straight-mineral-oil system, a vegetable oil system, and a constructional system, or a softener for resin. As a straight-mineral-oil system, process oil, such as an aromatic system, a naphthene system, and paraffin series, etc. are mentioned. As vegetable oil, they are castor oil, cottonseed cake oil, linseed oil, oleum rapae, soybean oil, palm oil, coconut oil, peanut oil, haze wax, pineapple oil, olive oil, etc.

Plasticizer : \*\* Phthalic ester, phthalic acid \*\* group ester, aliphatic dibasic acid ester, Various ester system plasticizers, such as glycol ester, fatty acid ester, phosphoric ester, and stearic acid ester, Plasticizers for NBR, such as an epoxy system plasticizer, other plastic plasticizers or a phthalate system, a horse mackerel peat system, a sebacate system, a phosphate system, a polyether system, and a polyester system.

\*\* Tackifier : various tackifiers, such as coumarone resin, coumarone-indene resin, phenol terpin resin, petroleum system hydrocarbon, and a rosin derivative (tackifier).

Oligomer : \*\* Crown ether, fluorine-containing oligomer, polybutene, Xylene resin, chlorinated rubber, polyethylene wax, petroleum resin, rosin spar varnish, Various oligomer, such as polyalkylene glycol diacrylate, liquid rubbers (polybutadiene, a styrene butadiene rubber, butadiene-acrylonitrile rubber, polychloroprene, etc.), silicone series oligomer, and the Polly alpha olefin.

Lubricant : \*\* Fatty acid system lubricant, such as hydrocarbon system lubricant, such as paraffin and a wax, higher fatty acid, and hydroxy fatty acid, Various lubricant, such as alcohol system lubricant, such as fatty-acid-amide system lubricant, such as fatty acid amide and alkylene screw fatty acid amide, fatty acid low-grade alcohol ester, fatty acid multivalent alcohol ester, fatty alcohol, polyhydric alcohol, polyglycol, and polyglycerol, metallic soap, and mixed stock lubricant.

[0014]In addition, latex, an emulsion, a liquid crystal, a bitumen constituent, clay, natural starch, sugar and also a silicone oil of an inorganic system, phosphazene, etc. can be used. Animal oil, such as beef tallow oil, lard, and horse oil, \*\*\*\*, fish oil, honey, fruit juice, chocolate, Dairy products, such as yogurt, a hydrocarbon system, a halogenated hydrocarbon system, an alcohol system, Organic solvents, such as a phenol system, an ether system, an acetal system, a ketone system fatty acid system, an ester system, a nitrogen compound system, and a sulfur compound system, or various medicinal properties, a soil conditioner, manure, petroleum, water, solution, etc. can be used.

[0015]As mentioned above, low molecule material is held between three-dimensional continuation reticulated skeletons which comprised an ethylene-propylene system copolymer (inside of internal communicated space), but a polymers network structure object of this invention. In this case, it is desirable to form a three-dimensional continuation reticulated skeleton with a little copolymers as much as possible.

[0016]When quantity of A and low molecule material is set to B for quantity of a copolymer which constitutes a three-dimensional continuation reticulated skeleton here, it is desirable for a weight fraction  $[(A/(A+B) \times 100)]$  of a copolymer to be 7 to 25% or less preferably 30% or less.

[0017]A polymers network structure object of this invention can be acquired when this copolymer mixes other ingredients in mixing requirements which can form three-dimensional continuation reticulated skeletal structure [ an ethylene-propylene system copolymer, low molecule material, and if needed ] for the specified quantity which were mentioned above.

[0018]Specifically, mixing preferably not less than 300 rpm of agitating speeds [ not less than 500 rpm of ] as not less than 1000 rpm still more preferably is recommended using high speed stirrers, such as a high shearing-die mixer. When not agitating at high speed, it is difficult to acquire uniform three-dimensional continuation reticulated skeletal structure of an ethylene-propylene system copolymer made into the purpose by a case where it mixes with a low speed, for example using a roll, a rotor type mixer, and a cylinder type mixer. A mixed temperature has the preferably desirable range of 150–200 \*\* 100–250 \*\*, and about 2 to 90 minutes of mixing time are preferably good for 1 to 120 minutes.

[0019]After performing mixing mentioned above, vulcanizing agents, such as sulfur and organic peroxide, can be mixed, or a bridge can be constructed by carrying out electron beam irradiation etc.

[0020]Thus, a polymers network structure object acquired has the structure where low molecule material mentioned above between three-dimensional continuation reticulated skeletons of an ethylene-propylene system copolymer in which meshes of a net were got blocked (inside of internal communicated space) was held.

[0021]As ethylene-propylene system rubber which is one ingredient of an ethylene-propylene rubber system constituent of this invention, the same EPR as the above-mentioned thing and also EPDM can be used. That is, it is preferred to use what has an ethylene content, a degree of crystallinity, Tm, and a number average molecular weight be [ the same as that of the above ] it.

[0022]A polymers network structure object of the (A) ingredient and the mixture ratio of ethylene-propylene system rubber of the (B) ingredient which were mentioned above, (A) A weight ratio of / (B) can control an elastic modulus in 0.3–8, and the desirable range in which it is good and wide 0.35–6, and to consider it as the range of 0.4–4 still more preferably by this. (A) A function as rubber of a rubber composition which will be obtained if a ratio of a polymers network structure object of an ingredient is too high may be spoiled, and on the other hand, if too low, the target rubber composition of a low elastic modulus may not be obtained.

[0023](A) A mixing method in particular of an ingredient and the (B) ingredient is not restricted, for example, can be easily blended with a common roll, a kneader, a mixer, a Banbury mixer, etc. In this case, the range of 40–100 \*\* can be used for a mixed temperature, and the mixing time can adopt 30–120 \*\* of conditions for 2 to 30 minutes preferably for 1 to 40 minutes.

[0024]The still more nearly following bulking agents may be blended with an ethylene-propylene system rubber composition of this invention if needed in addition to the above-mentioned ethylene propylene rubber and low molecule material in the case of mixing in addition to the (A) ingredient and the (B) ingredient. Namely, clay, diatomaceous earth, carbon black, silica, talc, barium sulfate, Calcium carbonate, magnesium carbonate, a metallic oxide, mica, graphite, Scaly inorganic fillers, such as aluminium hydroxide, various kinds of metal powders, a piece of wood, glass powder, Ceramic powder, granular thru/or granular thru/or natural or artificial staple fibers of a powdered solid bulking agent and other various kinds, such as powder polymer, continuous glass fibers (for example, straw, hair, glass fiber, metallic fibers, various kinds of other polymer fibers, etc.), etc. can be blended.

[0025]Since the ethylene-propylene system rubber composition of this invention can hold low molecule material like a lot of fluids, it can control an elastic modulus to a very low range. For

this reason, offer of goods in fields, such as a broad field of industry especially a household appliance, sporting goods, industrial machinery, a precision mechanical equipment, a transport-airplane machine, construction, engineering works, medical science, and leisure, is possible for this constituent. For example, buffer members, such as support members, such as holdown members, such as a sealant, packing, a gasket, and a grommet, mount, an electrode holder, and an insulator, a stopper, a cushion, and a bumper, are mentioned as vibration proof, damping, and shock absorbing material. As a shock absorber, sporting goods, such as a glove, a mitt, a golf club, and a tennis racket, It is suitably used as an object for shoes insoles, various toys, audio equipment, an electron and an electric appliance or a bed, a chair especially a medical bed that continues the posture same for a long time, a bed for cosmetics for hairdressing, a chair for playgoing, and a charge of vehicles material that receives vibration further.

[0026]It can use also for medical equipment, such as an artificial leg, an artifiical limb, a robot, an electrode material for electrocardiogram measurement, and an electrode material for low-frequency massage devices. It can use for an object for OA equipment, quake-absorbing rubber, a rubber cushion, a racing tire, etc. as super-low hardness rubber. In addition, it can use also for various kinds of molding materials as a low hardness plastic. Since control of discharge to the exterior of low molecule material is possible, it is used also for various sustained-release materials using discharge nature, such as an aromatic, a medical-application agent, and a functional material. In particular, it is suitable for various delivery rolls, such as OA equipment, such as a paper (Usuha object-like things other than paper are included) delivery rubber roll, for example, a copying machine, and a printer, a cash automatic transaction device (ATM), a money-changing machine, a counting machine, a vending machine, and a cash dispenser (CD).

[0027]

[Effect of the Invention]The ethylene-propylene system rubber composition of this invention can blend low-molecular-weight material so much, and since the holdout of low-molecular-weight material is good, can control an elastic modulus to the very low range, and can apply it to the various fields using a low elastic modulus.

[0028]

[Example]Although an example and a comparative example are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0029][Examples 1-3 and comparative example] The polymers network structure object was created by the presentation and combination which were shown in Table 1 (a comparative example is only low-molecular-weight material), EPDM shown in this and the table was mixed with the mixture ratio shown in the table, and the ethylene-propylene system rubber composition was obtained.

[0030]

[Table 1]

		実 施 例			比較例
		1	2	3	
高分子網状構造体	高 分 子 材 料	EPR	EPR	EPR	—
	数 平 均 分 子 量	26万	26万	26万	—
	エチレン含有量 (%)	74	78	74	—
	低 分 子 材 料	ポリブテン	パラフィン油	ナフテン油	ナフテン油
	E P R 混 合 率 (wt %)	20	15	10	—
E P D M		(1)	(1)	(2)	(1)
高分子網状構造体 / E P D M の重 量 比		1/1	2/1	1/1	1/1

EPDM (1) : ノーデル1040 (分子量22万)

EPDM (2) : JSR製EP33 (分子量25万)

[0031]The ethylene-propylene rubber constituent obtained in the example had good processability, and it was vulcanized gum with very few blot broths.

[0032]On the other hand, the ethylene-propylene rubber constituent obtained by the comparative example had poor processability, and its blot broth was very large.

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

[Brief Description of the Drawings]

[Drawing 1] It is a schematic diagram showing the cellular structure of the network structure object of this invention.

[Description of Notations]

- 1 Three-dimensional continuation network structure
- 2 Internal communicated space

---

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any damages caused by the use of this translation.

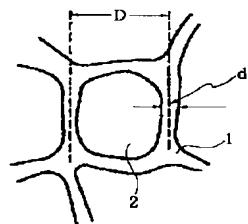
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DRAWINGS**

---

[Drawing 1]



---

[Translation done.]